

THE POLAROGRAPHIC REDUCTION OF
SOME ACETYLENIC LINKAGES

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PART I

INTRODUCTION

Electrolytic reduction at a dropping mercury electrode has been known for at least forty-eight years. This electrode was invented by Kucera¹⁰, who used it in investigations of the electro-capillary curve of mercury, in his attempts to find a single electrode of absolute potential. During his investigations he noticed some peculiarities of shape in the electrocapillary curve when the solution contained reducible substances. At his suggestion Heyrovsky made a study of these irregularities. Eventually this study led to the invention of the polarograph⁵.

The polarograph is an instrument for the electrolysis of solutions. Its distinguishing characteristic is the use of the dropping mercury electrode, which allows repeated tests of the same solution without changing the characteristics or concentration of the solution to any detectable extent. The Heyrovsky-Sargent Model XII Polarograph, as shown in Figure 1, photographically plots a graph of increasing transmitted current caused by a gradually increasing cathodic potential; the abscissa representing the potential and the ordinate the current. This graph is called a polarogram.

A relatively small current, called the residual current, flows through the circuit at any potential. This current is carried largely by the supporting electrolyte, which is a substance chosen for its resistance to reduction at the potentials used. The electrolyte has several functions. One is to reduce the resistance of the solution. Another is to keep the ionic strength, and therefore the ionic activities, constant.

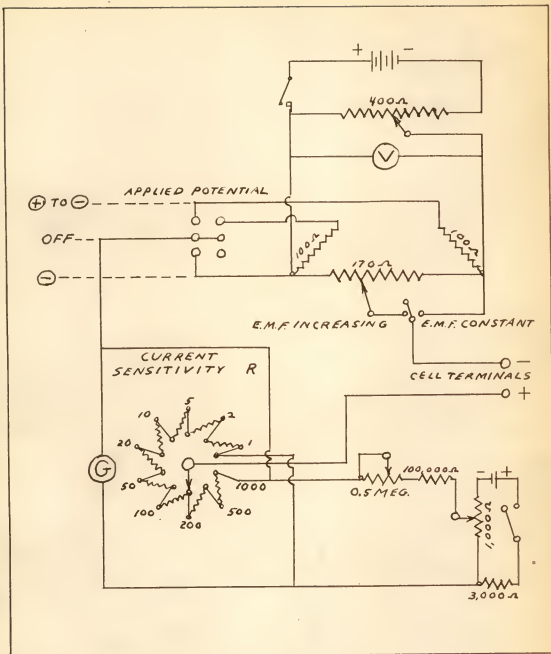


Figure 1

Wiring Diagram of the Sargent-Heyrovsky Model XII Polarograph

When possible, an electrolyte is chosen whose anion forms an insoluble mercurous compound, thereby keeping the anode process and the anode potential constant. The solution of the supporting electrolyte is commonly 0.1 N.

When the increasing cathodic potential reaches the reduction potential of some ion or compound in the solution, the current increases, producing a wave. The height of the wave gradually approaches a limiting value as the potential continues to increase. The height of the wave above the residual current is known as the diffusion current or i_d , and is characteristic of the concentration of the reducible substance. The potential at which the reduction takes place is characteristic of the nature of the reducible substance.

A polarogram can be made in five minutes, once the solution is prepared, thus allowing a quick qualitative and quantitative analysis. The accuracy of the quantitative determinations range from one to five-per cent, depending on the concentration.

This reduction potential was determined in any of several different ways in the past⁹. One was the tangent method, widely found in older literature, in which the reduction voltage was taken as the applied e. m. f. corresponding to the point where a 45° line would be tangent to the curve. Another method¹⁶ was to record the applied e. m. f. at the point where the curvature of the reduction curve was greatest. A third was to use the value of the applied e. m. f. at which an increase of 10 millivolts caused an increase of current of 0.019 microamperes (Shikata). Muller's comment¹³ is pertinent: "The most outstanding shortcomings of these methods are that these potentials change with the concentration of

the reducible substance, with the sensitivity of the galvanometer, and with the drop time and the rate of flow of the mercury."

Since the later work of Heyrovsky and Ilkovic^{6,7}, the overwhelming majority of reports of reduction potentials are in terms of the half-wave potential, symbolized by $E_{\frac{1}{2}}$. To evaluate $E_{\frac{1}{2}}$, a straight line is drawn as an extension of the residual current line. Another line parallel to this one is drawn through the peak of the curve. A line perpendicular to the base is drawn between the two parallel lines in a location such that the wave bisects the perpendicular. The e. m. f. at the point of bisection is called the half-wave potential, and can be determined accurately to ± 0.01 volt.

The importance of the half-wave potential is that it is a constant value, unaffected by changes in concentration of the reducible substance, for many substances, i. e., metals which form amalgams, reducing reversibly to the metal at the cathode. Irreversible reactions, such as the reduction of certain ions involving large over-voltages, may or may not have half-wave potentials independent of concentrations. Reactions involving reduction of ions from one oxidation state to another have constant $E_{\frac{1}{2}}$, while reduction potentials of metals not forming amalgams vary with concentration. However, these variations in $E_{\frac{1}{2}}$ are small, being of the order of magnitude of 0.05 volts for a concentration change of fifty-fold, for a reduction involving two electrons. An organic reduction may vary widely in the values of $E_{\frac{1}{2}}$ obtained, depending on solvent, other ions present, and the pH. Variations in electrolyte have no effect on a reversible organic reduction⁹.

The reduction of an organic compound, nitrobenzene, was carried

out as early as 1925 by Shikata¹⁷. He followed this with work on isovaleraldehyde¹⁸, pyridine¹⁹, and nicotinic acid²⁰. These and other investigations by him, his co-workers, and others established the polarograph as a valuable instrument for the organic chemist.

However, there is to date only one instance recorded of the reduction of acetylenic linkages¹¹. This is possibly due to the earlier lack of a supporting electrolyte that would not reduce at the high voltages needed. As late as 1945 it was reported²² that tetramethyl ammonium ion, used as the bromide, was the most stable of the electrolytes, with a tangent reduction potential of -2.93 volts, measured against the saturated calomel electrode (S. C. E.), the usual reference electrode. This reduction potential would allow determinations to be made at no higher voltage than the beginning of the reduction wave, about -2.5 volts vs. the S. C. E. It is now known that the use of tetrabutyl ammonium ion, in the form of the iodide, will allow determinations as high as -2.8 volts vs. the S. C. E.

An isolated double or triple bond cannot be reduced polarographically. However, such a bond conjugated with a carbonyl group or in a heterogeneous nucleus such as pyridine or quinoline can be reduced⁹. Phenyl-substituted olefines or acetylenes can also be reduced. This is in general agreement with the theory of resonance, as stated in a crude form by Kekule⁸ as early as 1872 and elaborated by Heisenberg⁴, Pauling¹⁵, and others. Essentially the theory is that a bond, which may have more than one form or electronic arrangement, does not exist in any one form,² but as an average of the different forms, the strength of the bond increasing with the number and probability of the different forms. The sub-

stitution of a group having a large number of electrons would tend by electrical force to settle the bond into predominantly a single form, thereby weakening it. Introduction of a second group of electrons, whose force would oppose that of the first group, should then allow more resonance and strengthen the bond.

Besides the relative bond strengths, the polarograms should give, by their shapes, information about the mechanism of the reaction involved. It has been previously established²¹ that a correction factor is needed in the Nernst type equation to allow for the adsorbability of certain molecular products. Information on the size of this adsorption factor, as well as an indication of the order of the reaction, may be obtained from the first and second derivatives of the modified Nernst equation, using the points of inflection and slopes of the curves²³. It is the purpose of this work to show, as far as possible, the mechanism of reduction and the extent of the effect of the changing electron groups on the resonance of the bonds.

PART II

EXPERIMENTAL

The polarograph used was a Sargent-Heyrovsky Model XII, which records the curves photographically. The cell was of a simple type, made from a 25 ml. Erlenmeyer flask. Sensitivity of the instrument was listed as 0.0087 microamperes per millimeter, at a shunt ratio of 1:1. However, it was found that wave heights of a series of solutions were not strictly proportional to the shunt ratios at the different concentrations, the variations being up to ten per cent. Therefore all comparisons are listed in millimeters of wave height, the shunt ratio or sensitivity being specified in each instance.

Mercury was purified by passage of fine droplets through dilute nitric acid, dilute sulfuric acid, and distilled water, followed by distillation at a pressure of about 2 mm. The conventional mercury pool, covering the bottom of the cell, served as the anode.

Air was removed from the solution by the usual method of bubbling with nitrogen for 15 minutes. The nitrogen was previously saturated by bubbling through a flask of water, so that it would not appreciably change the concentration of the solution. Other than this, the nitrogen was used as it came from the tank. A 600 ml. beaker of water, in which the cell was placed, was used as a thermostat.

In order to get a smooth curve, suitable for analytical purposes, the drop time was made much smaller than usual, e. g., 0.807 seconds at $E = -1.45$ volts vs. S. C. E. However, by the time the diffusion current was reached the drop time was much too small to be deter-

mined. This small drop time was obtained by using a mercury column of 720 mm. height.

As a general rule, accurate to within 3 per cent,

$$i_d = km^{2/3}t^{1/6}$$

for different capillaries under the same conditions or for one capillary under different pressure conditions, where k is a proportionality constant, m is the weight of mercury flowing in mg. sec.⁻¹, and t is time in seconds. It is therefore desirable to give data for m and t , to enable other workers to reproduce the conditions. Values for t could not be determined when i_d was reached. On open circuit, however, it was found that $m = 8.949$ mg. sec.⁻¹ and $t = 0.9187$ sec.

At various times, different concentrations of ethanol in water were used. All such solutions are shown as per cent ethanol by volume, the remainder being understood as water.

Two different supporting electrolytes were used during the course of the experiments. The first, tetramethyl ammonium bromide, was obtained from The Matheson Company. As obtained, a strong amine odor indicated the presence of impurities. The quaternary was purified by recrystallizing several times from hot 80 per cent ethanol, followed by several more recrystallizations by dissolving in 95 per cent ethanol and precipitating with diethyl ether. When this quaternary was polarographically pure, it would remain so from a week to several months in the solid state, but for not more than three days in solution. This electrolyte was used as a 0.1 N solution in water.

The other supporting electrolyte was tetrabutyl ammonium iodide,

obtained from the Eastman Kodak Company and also from the Commercial Solvents Corporation. At first it was purified by dissolving in 95 per cent ethanol and precipitating with peroxide-free diethyl ether. Later, when a larger supply was available, it was recrystallized from hot water. It remained pure for not more than three days in the crystalline form, and for not more than a few hours in solution. This electrolyte was necessarily used instead of tetramethyl ammonium bromide, with the compounds having higher reduction potentials. Since this electrolyte is soluble to the extent of only 0.07 N in water, it was prepared as a 0.1 N solution in 50 per cent ethanol as solvent.

Several aliphatic tertiary amines, each with an acetylenic linkage in one group, were available from previous research in the department¹⁴, as well as some triethyl allyl ammonium bromide³.

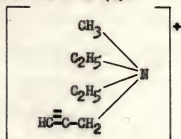
Preliminary tests on diethyl propyn-2-yl amine, in 50 per cent ethanol with 0.1 N tetramethyl ammonium bromide as a supporting electrolyte, showed a definite reduction wave. However, the irregularity of the wave indicated a relatively large quantity of impurities. It was decided to quaternize the amines, thereby producing compounds which probably could be purified with comparative ease by conventional methods of recrystallization.

The unsaturated quaternaries were easily formed. They are listed in Table I, each with a number, by which it will hereafter be identified. There is also shown a typical structural formula. Compound (I) was formed by bubbling methyl bromide through a warm solution of diethyl propyn-2-yl amine in diethyl ether. The compound began to precipitate within a few seconds. Compounds (II), (III), (IV), and (V) were

TABLE I

Number	Name of Compound	% Halide	
		Found	Theoretical
I	Methyl diethyl propyn-2-yl ammonium bromide	38.17	38.78
II	Triethyl propyn-2-yl ammonium bromide	36.09	36.29
III	Diethyl n-propyl propyn-2-yl ammonium bromide	33.42	34.12
IV	Diethyl n-propyl propyn-2-yl ammonium iodide	45.05	45.13
V	Diethyl n-butyl propyn-2-yl ammonium bromide	29.34	32.20
VI	Ethyl di-n-propyl propyn-2-yl ammonium bromide	32.21	32.20
VII	Tri-n-propyl propyn-2-yl ammonium bromide	30.40	30.49
VIII	Di-n-propyl n-butyl propyn-2-yl ammonium bromide	28.72	28.93
IX	Triethyl n-butyne-2-yl ammonium bromide	33.73	34.12
X	Triethyl n-pentyne-2-yl ammonium bromide	31.86	32.20
XI	Triethyl n-hexyne-2-yl ammonium bromide	29.93	30.48
XII	Triethyl n-heptyne-2-yl ammonium bromide	27.80	28.93
XIII	Triethyl n-octyne-2-yl ammonium bromide	27.44	27.53
XIV	Triethyl allyl ammonium bromide	33.70	35.96

Structural formula of (I).



formed from the same amine by refluxing it in each case with an excess of the appropriate alkyl halide. Compounds (VI), (VII), and (VIII) were similarly formed from di-*n*-propyl propyn-2-yl amine. The iodides corresponding to compounds (I), (VI), and (VII) were also formed, but were not used due to the lesser stability of the iodides in general.

Compounds (IX) through (XIII) were similarly formed from a homologous series of amines, diethyl butyn-2-yl amine through diethyl octyn-2-yl amine. In each case the quaternary was insoluble in the excess of ethyl bromide and crystallized or separated as a viscous liquid. These liquids would usually form crystals within a few hours, especially if subjected to vacuum. Compound (V) never did crystallize, but remained as a molasses-colored very viscous liquid, in spite of such vigorous treatment as storing in a vacuum dessicator in the ice room for three days, treating with "dry ice", and other methods.

Increasing weight of the molecules increased the time needed for formation, even though the refluxing temperature also increased, and also increased the tendency to form liquid products. Compounds (IX) through (XIII) were deliquescent, this property becoming more active with increasing molecular size. Drying could be done only by vacuum, as the compounds absorb water readily even when stored in tightly capped sample bottles in a dessicator with calcium chloride.

Purification of the compounds was a major problem. For compounds (I) and (II), the most efficient method seemed to be dissolving in aniline and reprecipitating with dioxane or amyl acetate. This, however, gave a finely divided precipitate which was difficult to filter. This solvent mixture was not effective on the larger molecules, but

would leave them in solution.

These two compounds, as well as all of the others, were also purified by dissolving in 95 per cent ethanol and reprecipitating with ether. The precipitate might be flocculent, in small flakes, in large flakes, in granules, or as a heavy liquid, depending on factors which were never understood. The larger molecules required a much greater excess of ether for precipitation. The compounds varied in color from a very light yellow to a deep brown. After each two or three recrystallizations a small quantity of a chocolate-colored sediment, which was insoluble in all of the usual solvents, was found. A rather large quantity of this substance was formed on one occasion, when some (II) was allowed to remain in contact for a week with a dioxane-aniline solution. This sediment was believed to be a polymerization product. ¹⁶

All of these compounds are very unstable. On one occasion compounds (VI) and (VII) remained polarographically pure for three days, so that curves could be run at several different concentrations. None of the others ever remained pure for as much as one day. The ones of lower molecular weight were less stable. Compound (II) was recrystallized more than thirty times, from ethanol and ether, before it gave a wave sufficiently clear for the accurate determination of the half-wave potential. Only twice in the course of the experiments was this compound pure enough to give waves on which the point of inflection could be determined. The best method of purifying it and (I) was found to be: recrystallization of a newly synthesized batch ten or fifteen times, as rapidly as possible, from ethanol and ether, followed by two or three recrystallizations from aniline and dioxane; it might then be pure enough

for use, or might not; if not, repeat the process, trying a small quantity in the polarograph from time to time. More than seven hundred polarograms were made in the course of this investigation.

When the polarograph showed the compound to be polarographically pure, it was considered advisable to make all determinations as soon as possible. In the course of more than twelve hundred recrystallizations no routinely infallible procedure for purification was ever developed, nor was it ever possible to predict the number of treatments needed at any time to purify any one compound.

Proof of composition of each compound was furnished by Volhard analyses for ionic halide. Results of these analyses are shown in Table I. It will be noted that in general the per cent ionic halide found is less than the theoretical per cent present. This is considered to be caused either by the formation of some saturated compounds or by the adsorption by the compound of some decomposition products from the original solution. Supporting evidence for the latter theory is the fact that some of the compounds became lighter in color upon repeated recrystallization. Analysis of the liquid form of (V) indicated relatively large quantities of either solvent or impurities.

With compounds (I) through (VIII) and (XIV), the method used was as follows: a solution of 0.1 N tetramethyl ammonium bromide was prepared in water, using a volumetric flask, and 10 ml. portions withdrawn. The appropriate weight of the reducible compound was added to make the desired concentration of solution. The volume of the sample itself was ignored. This was found, by experiment, to cause an error of less than one per cent in volume or concentration, which was within the

limits of reproducibility of the wave height. When experiments proved the compounds stable enough over a period of time to allow use at several concentrations, as in compounds (VI) and (VII), solutions were made up volumetrically of 0.2 N electrolyte and 0.02 N compound and the two combined in the proper proportions with each other and with water to give the desired solution, using a Mohr pipette.

Compounds (IX) through (XIII) could not be purified sufficiently to allow quantitative work. For work with these compounds, the supporting electrolyte used was tetrabutyl ammonium iodide, 0.1 N in 50 per cent ethanol. In each case enough of the compound was added to give a wave of 50 mm height or above at sensitivity 50, that is, the shunt ratio at which 1/50 of the current in the circuit passes through the galvanometer. Obviously only the general trend of voltages could be determined.

All determinations were made at 25⁰ Centigrade plus or minus one half of a degree. The temperature coefficient of polarographic waves are very minute and therefore no measurable error was introduced. All reports are based on averages of all determinations at any one concentration and sensitivity.

Each curve was checked at two different points for applied voltage, using a "Queen" Standard Potentiometer, Model E-3040-T, made by the Gray Instrument Company. The potential of the anode pool against a saturated calomel electrode was then determined, and all voltages are listed against the S. C. E. It was experimentally determined that the solution was so little affected by the electrolysis that the anode potential remained unchanged after fifteen curves had been produced. The potential of the anode has been shown to remain constant during an electrolysis, if the solution contains halide ions¹².

PART III

DISCUSSION

All of the compounds except (III), (IV), and (XIV), gave well-defined reduction waves, with values of $E_{\frac{1}{2}}$ of above -1.6 volts. The failure of compound (XIV) to give a reduction wave in the polarograph indicates that the olefinic linkage would not reduce at the voltages available. This in turn indicates that the reduction of (II), a compound differing from (XIV) only in the presence of an acetylenic linkage rather than an olefinic one, is a two electron reaction giving as an end product the olefin, rather than a saturated group.

It was originally planned to make all determinations at several values of pH, using, as buffers, organic acids with their tetramethyl ammonium salts, since all other cations reduce below the potential desired. Both tetramethyl ammonium citrate and monotetramethyl ammonium phosphate were prepared, but gave well-defined waves of polarographically pure substances reducing in the range of 2 to 2.2 volts vs. S. C. E. The buffer project was therefore abandoned. It should be noted that Laitinen and Wawzonek¹¹ found that variations in pH had no effect on the half-wave potential of some phenyl-substituted olefins.

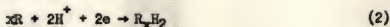
The general equation for the polarograph is

$$E_{\text{applied}} = E_{\text{anode}} - E_{\text{cathode}} + iR \quad (1)$$

E_{anode} and iR are kept constant by the presence of the supporting electrolyte.

The equation of the cathode reaction for the present series of

compounds may be written



and therefore

$$E_{\text{cathode}} = E^0 - \frac{RT}{2F} \ln \frac{a_{R_xH_2}}{a_R^x a_H^2} \quad (3)$$

By substituting (3) in (1), and grouping constants, we obtain

$$E_{\text{applied}} = E^{0'} + \frac{RT}{2F} \ln \frac{a_{R_xH_2}}{a_R^x a_H^2} \quad (4)$$

The activity coefficient is a constant, kept so by the excess of supporting electrolyte. By rewriting (4) as producing OH^- in water solution, rather than consuming H^+ , and again grouping all constants, including K_w , we obtain

$$E_{\text{applied}} = E^{0''} + \frac{RT}{2F} \ln \frac{C_p C_{OH^-}^2}{C_r^x} \quad (5)$$

with p and r representing products and reactants, respectively.

As the product is not an amalgam, a factor must be introduced to correct for adsorption effects²¹. The reduced form is considered to be largely present on the surface of the mercury drop, in equilibrium with the immediately surrounding solution. By applying the Freundlich empirical equation to the products,

$$C_{\text{solution}} = KC_{\text{surface}}^{\frac{1}{n}} \quad (6)$$

the term \underline{z} representing the adsorption exponent, a parameter greater than one, and \underline{K} is a distribution constant.

Since

$$C_{\text{surface}} = ki \quad (6)$$

By substitution

$$C_{\text{solution}} = K(ki)^{\underline{z}} \quad (7)$$

when \underline{k} is a proportionality constant and \underline{i} is the current, at any time, in excess of the residual current.

Also, at any time, by well-known polarographic derivations, since the reactant present is equal to the original concentration minus the amount reduced, \underline{k}' being a proportionality constant,

$$C_r = k'(i_d - i) \quad (8)$$

and since the OH^- formed is, from the nature of the reaction, $\frac{2}{x}$ times the reactant used,

$$C_{\text{OH}^-} = \frac{2}{x}(C_r^0 - C_r) \quad (9)$$

And

$$C_r^0 = k'i_d \quad (10)$$

It follows, by substituting (8) and (10) in (9), that at any time

$$C_{\text{OH}^-} = \frac{2}{x} k' i \quad (11)$$

By substituting (7), (8), and (11) in (5) and combining constants, we obtain

$$E = E^{0'''} + \frac{RT}{2F} \ln \left[\frac{K' i^{\underline{z}+2}}{(i_d - i)^{\underline{x}}} \right]$$

Dividing both numerator and denominator by the constant $i_d^{\underline{z}+2}$ gives

$$E = E^{o''''} + \frac{RT}{2F} \ln K' \frac{\left[\frac{1}{i_d}\right]^{z+2}}{\frac{1}{i_d^{z+2-x}} \left[\frac{i_d - 1}{i_d}\right]^x} \quad (12)$$

Grouping all constants gives

$$E = E^{o''''} + \frac{RT}{2F} \ln \frac{\left[\frac{1}{i_d}\right]^{z+2}}{\left[1 - \frac{1}{i_d}\right]^x} \quad (13)$$

This equation, though usable, is unwieldy, so we introduce and substitute the term $u = \frac{1}{i_d}$, giving the modified form of the Nernst equation as used by polarographers

$$E = E^* + \frac{RT}{2F} \ln \frac{u^{z+2}}{(1-u)^2} \quad (14)$$

Differentiating this equation gives

$$\frac{dE}{du} = \frac{RT}{2F} \left[\frac{z+2}{u} + \frac{x}{1-u} \right] \quad (15)$$

$$\frac{d^2E}{du^2} = \frac{RT}{2F} \left[-\frac{z+2}{u^2} + \frac{x}{(1-u)^2} \right] \quad (16)$$

By finding the slope at the half-wave, where $u = \frac{1}{2}$, for equation (15), and using the value of u at the point of inflection, where $\frac{d^2E}{du^2} = 0$, for equation (16), we obtain the forms to be used in this problem

$$\frac{dE}{du} = \frac{RT}{F} (z + x + 2) \quad (17)$$

and

$$\frac{s + 2}{u^2} = \frac{x}{(1-u)^2} \quad (18)$$

The polarographic slope, $\frac{dE}{du}$, is the reciprocal of the slope as usually expressed and is determined by the following method. On each curve, a tangent is drawn at the half-wave potential, the tangent acting as the hypotenuse of a right triangle. A vertical line drawn to the same point, its length equal to i_d , acts as the altitude of the triangle. The base of the triangle, expressed in volts, is the polarographic slope.

Using values of $\frac{dE}{du}$ as calculated above and values of u at the points of inflection as determined from the curves, the values of x and z in Table 2 were calculated. The slopes and shapes of curves of various compounds were similar, as shown in Figure 2. Inflection points were indistinct, similar to those of peroxide waves. Figure 3 compares waves of compound (II), H_2O_2 , and Gd^{++} . All waves were at sensitivity 50, height 70 to 80 mm. All were plotted as $\frac{dI}{dE}$ versus E . The values for $E_{\frac{1}{2}}$, u at the point of inflection, and slope are average values obtained from at least five curves in each instance.

For the series of compounds (I) through (VIII), in which the unsaturated group was held constant as propyn-2-yl while the saturated groups were varied, there was a linear relation between the total number of carbon atoms in the saturated groups and the half-wave potential, as shown in Figure 4. However, when one saturated group was as much as two carbon atoms longer than others, this relation did not hold, as evidenced by compound (V). This indicates that a dense concentration of electrons has the effect of limiting resonance at the unsaturated linkage, thereby

TABLE II

Gmpd.	Carbons in sat- urated groups	Conc.	Sensiti- vity	i_d	E_1 — s	U at infl.	Slope	\bar{z}	\bar{x}
I	5	1×10^{-2}	100	101	-1.990	0.632	0.440	10.5	4.06
			200	50					
II	6	1×10^{-2}	100	60.8	-1.917	0.673	0.434	11.0	3.81
		6×10^{-3}	50	74.7	-1.895	0.642	0.422	13.1	3.87
			100	35.8					
III	7	1×10^{-2}	50	No reduction wave					
IV	7	1×10^{-2}	50	No reduction wave					
V	8	+	50	+	-1.850	+	+	+	+
VI	8	1×10^{-2}	50	87.6	-1.815	0.650	0.520	13.6	4.50
			100	42.0					
		8×10^{-3}	50	64.1	-1.804	0.627	0.512	12.6	5.20
			100	30.5					
		6×10^{-3}	20	124.1	-1.813	0.615	0.479	11.2	5.28
			50	46.4					
			100	21.0					
		4×10^{-3}	20	78.2	-1.802	0.602	0.473	10.7	5.61
			50	31.4					
			100	15.8					
		2×10^{-3}	10	67.7	-1.805	γ	γ	γ	γ
			20	39.8					
			50	13.5					

See legend on page 21

Continuation of Table II

Cmpd.	Carbons in sat- urated groups	Conc.	Sensiti- vity	i_d	$E_{1/2}$	U at infl.	Slope	\bar{x}	\bar{z}
VII	9	1×10^{-2}	50	63.0	-1.747	0.621	0.526	12.9	5.34
			20	145.5	-1.751	0.605	0.529	12.2	6.21
			50	57.5					
		8×10^{-3}	20	129.0	-1.761	0.606	0.528	12.2	6.01
			50	51.2					
			20	111.0	-1.757	0.613	0.529	12.6	5.83
		6×10^{-3}	20	97.0	-1.762	0.609	0.520	12.8	5.32
			50	35.2					
			20	82.0	-1.755	0.597	0.512	11.5	5.98
		5×10^{-3}	50	30.5					
			10	134.5	-1.754	0.582	0.521	11.0	6.37
			20	66.0					
		4×10^{-3}	50	24.5					
VIII	10	1×10^{-2}	50	56.0	-1.681	%	%	%	%
			100	25.0					
		6×10^{-3}	20	90.0	-1.675	%	%	%	%
			50	35.0					

* Could not be determined, due to slight wave irregularities.

γ Could not be determined, due to wave irregularities at low concentrations.

% Could not be determined, due to wave characteristics.

All Polarograms Start at -1.2 Volts

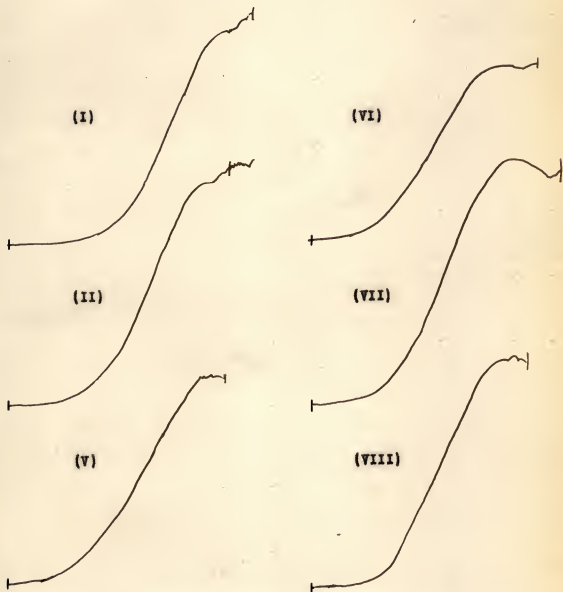


Figure 2
Comparison of Polarograms of Compounds Containing
the Propyn-2-yl Group

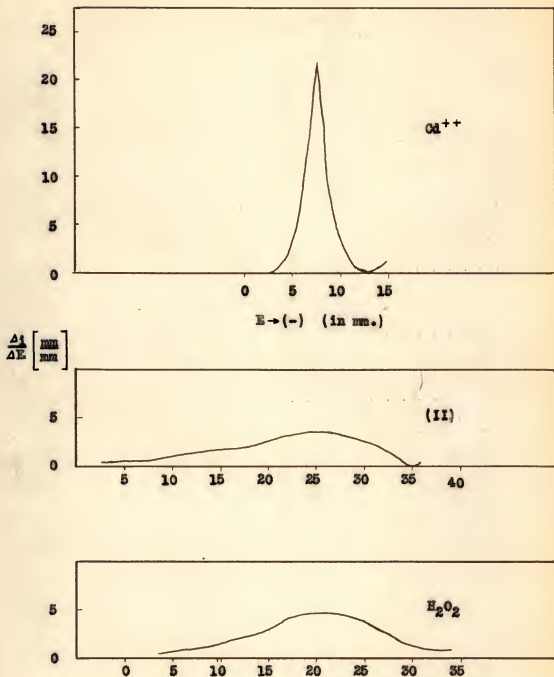


Figure 3

Comparison of Differentiated Polarograms of Compound (III),
Cadmium, and Hydrogen Peroxide

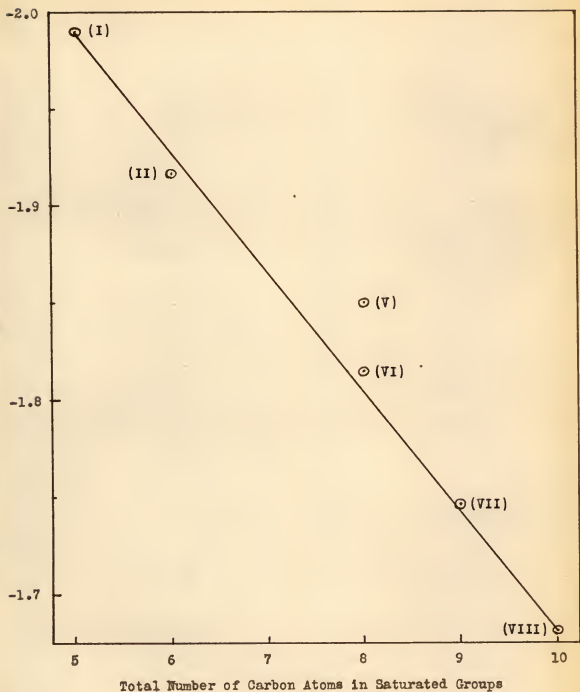


Figure 4

Effect of Number of Carbon Atoms in Saturated Groups on the
Half Wave Potential

making reduction easier. However, when one group was unduly lengthened, it blocked out the effect of the other groups, thus allowing a stronger bond.

The diethyl n-propyl propyn-2-yl ammonium ion, in compounds (III) and (IV), gave no reduction wave. The reason for this was not determined.

For the series of compounds (IX) through (XIII), no quantitative determinations were made, due to the persistent presence of impurities. In this series, with compound (II) included, the saturated groups were held constant at triethyl, while the unsaturated group was lengthened gradually from propyn-2-yl to octyn-2-yl. Curves obtained from these compounds indicate clearly, as shown in Figure 5, that the addition of carbon atoms affects the bond strength noticeably up to pentyn-2-yl. After that, little if any effect is noticeable. This is in agreement with the theory that the lengthening of the chain opposes the effect of the nitrogen group, thereby allowing more resonance and strengthening the bond. The limit of the effect is in agreement with the theory¹ that each carbon atom added to the chain would have approximately one-third of the effect of the preceding one. Therefore only three carbon atoms beyond the triple bond would have much effect.

The values of \bar{x} indicate considerable polymerization. It has been previously found² that olefinic quaternaries will polymerize. This is the first indication, however, that acetylenic quaternaries will polymerize, when they are subjected to partial reduction. The irregularities in values of \bar{x} are partially due, at least, to the difficulty of reading exact values of the points of inflection. However, they are

All Polarograms start at -1.5 Volts



Figure 5

Comparison of Polarograms of Compounds Containing
Various Unsaturated Groups

also probably due in part to being the average values of a large number of reactions.

As was to be expected from the calculated values of Σ , adsorption effects were marked, approaching detergent properties in the heavier molecules. In solutions of (VIII), especially, the mercury drops at times did not coalesce, but remained as separate drops resting on the anode pool. In the same solution the bubbling nitrogen caused the formation of persistent frothing on the surface.

Kolthoff and Lingane⁹ have stated that the drop time should be between three and six seconds, for the concentration to be proportional to the diffusion current at low concentrations. However, this straight line relation was found to hold for compounds (VI) and (VII), using a much smaller drop time, as shown in Figure 6. Variations are less than 5 per cent, or within the limits of accuracy for work at these concentrations. No other compounds were ever in a pure state long enough to make tests at varied concentrations.

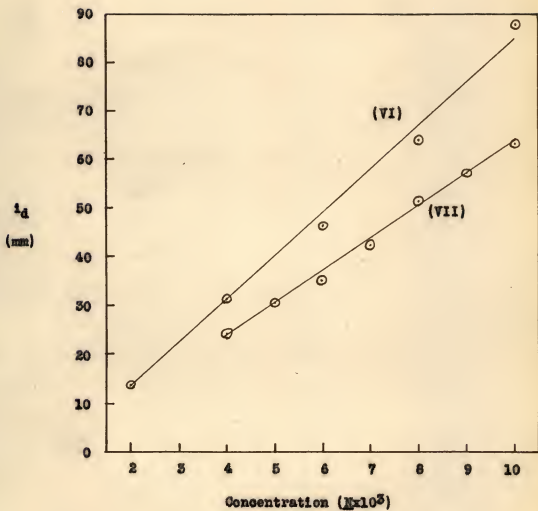


Figure 6
Effect of Concentration on the Diffusion Current

PART IV

SUMMARY

Two series of unsaturated quaternaries were formed, each compound containing an acetylenic linkage. In one series, the unsaturated group was held constant, and the saturated groups varied. In the other series, the saturated groups were held constant and the unsaturated group lengthened. It was found that increasing the sizes of the saturated groups lowered the reduction potential of the unsaturated linkage, as measured by the polarograph, while lengthening the unsaturated group strengthened the triple bond. These results are in agreement with the theory of the effect of resonance on bond strength.

Analysis of the polarograms showed a multi-molecular reaction, the number of molecules involved increasing with decreasing strength of the unsaturated bond. The compounds were surface active to a high degree, approaching detergents in their effect.

A much shorter drop time than conventional was used. Nevertheless, the diffusion current was proportional to the concentration in the range of 10^{-2} to 10^{-3} N.

PART V

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BIOGRAPHICAL NOTES

The author was born in Eastman, Georgia, August 20, 1911.

His undergraduate studies were pursued at The Citadel, Charleston, S. C., and he received his B. S. degree from that institution in June 1931.

He entered Graduate School at the University of Florida in the Summer School of 1938. His studies were interrupted by the war, but he re-entered in February 1946 and has been in attendance since that date. He received the M. S. degree in 1948, studying under Dr. Fred H. Heath.

From 1931 to 1938 he taught in various high schools in Georgia and Florida, and from 1940 to 1946 served as an officer in the Air Corps. He held positions in the Department of Chemistry, University of Florida, as Graduate Assistant, Teaching Assistant, and Interim Instructor, Part Time, successively. He is a member of Gamma Sigma Epsilon and the American Chemical Society.

COMMITTEE REPORT

This dissertation was prepared under the direction of the Co-Chairman of the Candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Date June 14, 1951

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